THEORETICAL CONSIDERATIONS FOR LIQUID PHASE SINTERING AND SOLIDIFICATION IN THE SPACE ENVIRONMENT

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ABSTRACT

Many types of materials processing experiments planned for operation in the space environment involve crystal growth, metals joining, solidification or sintering. Complete characterization of the liquid-solid interface is essential for analysis of these experiments. The necessary interface condition of wetting is effected by both zero gravity and the composition of the environment. Wetting is achieved by decreasing the solid-liquid interface energy through preferential adsorption of one of the constituents in the liquid on the solid surface and/or by diffusion fluxes. Adsorption of the environmental gases on the solid surface prior to exposure to the liquid phase will decrease the solid-vapor interfacial energy and inhibit the wetting process. Sintering and joining processes involve two steps: First a solid-solid phase and then a liquid-solid phase. Analysis of these processes shows that the first step is dependent on diffusion coefficients, vacancy concentrations in the bulk, surface energy and contact geometry, in addition to time and temperature. The second step is dependent on surface adsorption controlled by crystal faceting, grain boundary grooving, and thermal etching. Knowledge of these specific material properties from laboratory experiments will help to define the specific effects of gravity separated from the effects of the gaseous environment in space.

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I. INTRODUCTION

The zero or negligible gravity condition achieved in a space station (SS) can be used in material processes which simultaneously involve liquid and solid phases. The two phases may tend to separate due to density differences under the influence of gravity but will not tend to separate in space. This fact has been discussed previously in several proposals to do crystal growth, metals joining, casting solidification, or sintering in space. One such process, liquid phase sintering, is discussed in detail here but much of the analysis is applicable to the other processes mentioned above. Liquid phase sintering occurs when a mass of small particles of different compositions is heated above the melting temperature of one of the compositions so that all the particles become bonded into a solid mass on cooling.

Liquid-phase sintering of powder compacts is common not only to metal composites such as iron-copper, but to cermets and ceramic porcelains. In many cases involving the more refractory materials such as carbides and borides, it is only in the presence of a liquid phase that the desired properties can be obtained. The most successful cermets developed to date are undoubtedly the cemented tungsten carbides. Although these possess poor oxidation resistance and high densities, properties which reduce their utility as structural components at elevated temperature, their wide application as cutting tools attests their unique properties of high hardness, strength, and toughness.

As an example some physical properties of selected liquid metals are shown in Table I. The solubility of carbon in these metals is shown because we are planning to demonstrate the effects of density in experiments using spherical carbon particles as the dispersed solid in the liquid metal. For the liquid phases the metal has been chosen. The composites Al-C and Ag-C would be studied to determine the effect of density difference between the liquid and solid phases. It can be seen that liquid Al has a density of 2.37 gm/cm^2 which is very close to that of carbon (2.22 gm/cm^3) while Ag has a density of 10.5 gm/cm^3 in the liquid state which is very much higher than that of carbon. On the other hand liquid Al has a surface energy of 920 $ergs/cm^2$ and liquid Ag of 923 $ergs/cm^2$. Use of these two material systems would demonstrate the effect of density on "liquid phase forming" at constant surface energy.

Before considering the parameters important to the sintering behavior of liquid-solid systems, it should be pointed out that for any sintering to take place, it is first of all necessary for the liquid to be retained within the compact. That is, adequate wetting is a necessary condition for liquid-phase sintering. It is, therefore, necessary

that consideration be given to the wetting phenomena and its relation to liquid-phase sintering under those conditions existing in a space station. In this case, a consideration of zero gravity as the only environment is erroneous. The total environment of SS includes (i) zero gravity, (ii) vacuum of 10^{-5} mmHg and (iii) residual gases. It is apparent that to fully understand the effects of zero gravity in the sintering process, or any other metallurgical process, one must separate those effects due to the inherent vacuum and residual gases since these may affect the degree of wetting obtained. In so doing it may be possible to ascertain the possible approaches for changing a system from a state of nonwetting to wetting. As discussed, density and surface wetting are the important variables in experiments leading to space materials processing. However it is vital that we define the environmental effects which cause variations in the surface wetting. The remainder of this discussion will emphasize the importance of our surface studies.

II. WETTING

Wetting may be discussed by analyzing the behavior of a liquid drop in contact with a solid surface as in Figure 1. The degree of wetting is measured by the contact angle θ . For $\theta > 90°$ a nonwetting condition exists while a wetting condition is described by $\theta < 90°$. The extent of wetting attained in any liquid-solid system is determined by the surface forces that act on the system to give a configuration having the lowest total surface free energy and thus minimizing the total free energy of the system. A vectorial analysis of the horizontal components of the surface forces gives the following expression for the contact angle:

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \qquad (1)$$

where γ_{SV}, γ_{SL} and γ_{LV} are the surface energies of the solid-vapor interface, solid-liquid interface and liquid-vapor interface, respectively.

Consideration of this equation leads to several relationships between the contact angle and the various surface energies. Table II contains a summary of the effect of these relationships. It is noted that the only way to change a nonwetting system to a wetting system is by decreasing the solid-liquid surface energy. It is thus important to consider the ways in which the liquid-solid interface energy can be reduced for improved wetting.

One process which can change or reduce the solid-liquid surface energy is the preferential adsorption of atoms or ions at the interface.[1] The preferential adsorption of nickel from Cu-Ni alloys in TiC surfaces is

an example of this effect. A detailed description of the adsorption problem will not be attempted here; however, it will be mentioned that in the Gibbs equation relating adsorption and interfacial energy a term representing the thermodynamic activity of the surface active constituent in the liquid is included. Further, the adsorption of this constituent is dependent on the microscopic site it occupies on the surface. Dislocation cores intersecting the surface, vacancy cluster configurations, edges of ledges, etc. all promote favorable energy exchanges leading to preferential adsorption.

It is for this reason that a detailed knowledge of the surface conditions and the mechanisms promoting those conditions in a space station environment are important. Our surface studies are aimed at providing such knowledge. It should be pointed out that extensive evidence exists showing the effect of vacuum environments on surface faceting, thermal etching, and grain boundary grooving. Each of these phenomena will affect an adsorption process and surface energies, and they will be discussed in detail later.

Another process which may lead to a lower surface energy, and thus improve wetting, is that of diffusion. For instance, when a liquid comes in contact with a solid in which there is appreciable solubility of the solid in the liquid, a diffusion gradient exists across the interface, and the apparent surface energy changes.[2] Since the surface energy is related to the composition changes resulting from diffusion, it would appear desirable to decrease the rate of diffusion and hence, increase the time required for equilibrium to be reached. This can be accomplished by having diffusion take place from the liquid into the solid. In practice this condition is realized in the Ni + Mo alloy - TiC system when the addition of molybdenum to nickel enhances the wettability of titanium carbide and lowers the liquid alloy - carbide surface energy. Studies have shown that molybdenum diffuses from the liquid phase into the titanium carbide. In a system such as this, the controlling process or mechanism would be diffusion in the solid i.e. molybdenum diffusion in the carbide. This diffusion is in turn related to vacancy concentration, dislocation densities, and other defect structures in the solid phase. The possibility of controlling this process by controlling the defect structure of the solid phase at and near the liquid-solid interface is one of the reasons for doing our vacancy study which will be discussed in more detail later.

An example of some liquid metals and carbon selected for studying the effects of wetting or surface energy at constant density is shown in Table III. The composites Sn-C and Zn-C have liquid phases with very similar densities but dissimilar surface energies (575.9 ergs/cm^2 for Sn and 773 ergs/cm^2 for Zn) and could be expected to show the effect of different liquid surface energies on the process. These metals have

relatively low melting points and thus the power requirements in the space laboratory would be minimal for this kind of experimentation.

III. ENVIRONMENT

At this point it is necessary to inject a note about the composition of the environment. The gaseous environment in the experimental chamber of the space station must be duplicated in the experimental chambers on earth because it will effect the solid-vapor surface energy which in turn effects the process. It is not enough to duplicate the total pressure. Duplication of the partial pressures of molecular and atomic oxygen, for example, is necessary. It will be most convenient to use the vacuum of space to provide ejection of entrapped gases, reduction of surface reactivity, and separation of the experiment from the cabin environment. However, these subtle compositional differences in the residual gas must be considered.[4]

IV. ADSORPTION OF ACTIVE GASES

If there is any change in the fraction of atomic to molecular oxygen, consideration must be given to possible adsorption phenomena and any effects these may have on the sintering process. It is advantageous to consider the sintering process as passing through two stages, i.e. the heating up or "initial" stage when only solid and gas phases are present and the liquid-phase stage when one of the solid phases becomes a liquid. In the initial stage we can treat the problem of adsorption by considering the Gibbs adsorption equation in the form:

$$d\gamma = -SdT - \Sigma \Gamma_i \, d\mu_i \qquad (2)$$

where γ is the specific surface free energy, S the entropy, T the absolute temperature, Γ_i the surface density of the i th component and μ_i the chemical potential of the i th component.[5] If we consider a solid surface (component 1) in equilibrium with a gas (component 2), then as the gas pressure p_2 is varied at constant temperature we have:

$$d\gamma = -kT \Gamma_2 \frac{dP_2}{P_2} \qquad (3)$$

The procedure is to invoke some analytical expression relating Γ_2 and P_2 and integrate equation (3). For these analytical expressions we choose (1) the Langmuir isotherm for a gas of atoms or molecules which do not dissociate and (2) the modification of the Langmuir isotherm for diatomic molecules which dissociate on adsorption. These are

$$\Gamma_2 = \frac{K P_2}{P_2 + P_0} \tag{4}$$

$$\Gamma_2 = \frac{K P_2^{1/2}}{P_2^{1/2} + P_0^{1/2}} \tag{5}$$

where K is a constant of the order of the number of adsorption sites per unit area, and P_0 is a characteristic pressure at which saturation effects set in. For these two cases integration of (3) gives, respectively,

$$\gamma = \gamma_0 - KkT \ln\left(1 + \frac{P_2}{P_0}\right) \tag{6}$$

$$\gamma = \gamma_0 - 2KkT \ln\left[1 + \left(\frac{P_2}{P_0}\right)^{1/2}\right] \tag{7}$$

where γ_0 is the surface energy at gas pressure $p_2 = 0$.

Equations (6) and (7) illustrate that the surface energy γ can change considerably for any gas which is sufficiently strongly adsorbed and that this change is a decrease of the surface energy.

For the space vacuum we can now predict that the presence of atomic oxygen will lead to the adsorption of these atoms on the surface of solid materials and that this adsorption will most likely lead to a lowering of the specific surface free energy of the solid. If this solid phase is then to be exposed to a liquid phase (as in the second sintering stage) we can predict, based on the decreased surface energy of the solid at the vapor-solid interface, that an increase in the contact angle of wetting will result. An increased contact angle means, in turn, that wetting during the space sintering operation would be decreased.

It thus becomes apparent that a knowledge of the complete environment of the zero gravity experiment is important if the true effects of a zero gravity are to be accurately ascertained from experiments involving liquid and solid phase combinations (as in liquid phase sintering). More specifically, the extent of the adsorption phenomena must be determined together with their quantitative effects on the wetting phenomena.

V. EFFECT OF HIGH TEMPERATURE AND VACUUM - THERMAL FACETING

One effect due to the combined action of vacuum and high temperature on a metal surface is thermal etching.[6] In this case one can observe two distinct phenomena (i) the formation of grooves at grain boundaries (a result of surface energy forces) and (ii) the surfaces of the grains show thermal faceting, which when fully developed is a simple surface structure consisting of facets usually of only two types of planes. One of the planes is of low Miller indices while the other is more complex and is of the orientation necessary to keep the average surface orientation parallel to that of the original surface. Thermal faceting can take place with metals or nonmetals, and close control of temperature and residual gas in the surrounding vacuum is required if consistent (reproducible) effects are to be observed.[7,8]

Thermal faceting is related to surface free energy in that the specific surface free energy of a crystal will vary with crystalline orientation. If orientations exist where the surface free energy is markedly low, smooth surfaces of intermediate orientations may reduce their total surface energy by breaking up into facets of the low-energy orientations. However, as the average surface orientations remains parallel to the original surface, the formation of facets is limited. At the point of minimum energy, a certain fraction of the surface will be covered with facets, and the surface between facets will be tilted with respect to the original surface and will not in general be of a low-energy orientation. However, the final faceted surface will have a lower energy than the initial smooth one.

The change in surface energy due to faceting will affect wetting. Therefore, this effect must be completely categorized if the response of sintering in zero gravity is to be understood. Also it is evident from the above that the usual assumption, i.e. "the solid surface energy remains constant" made in interpreting the wetting phenomena during liquid phase sintering cannot be applied in the case of sintering in a space environment.

VI. MASS TRANSPORT AND DIFFUSION IN INITIAL SINTERING STAGE

Thus far it has been pointed out (Section II) that adsorption and diffusion phenomena occuring at the solid-liquid interface during liquid phase sintering can influence the degree of wetting and thereby control the sintering process. It has been further pointed out, Section IV, that in the initial stages of the sintering process, when only solid and gaseous phases are present, adsorption of the gases on the solid surface can effect surface energies and thereby effect the wetting phenomena. Still another phenomenon must be considered with regard to this initial stage. It is the mass transport and diffusion

that results in some degree of sintering in the solid state. It is important to consider this phenomenon because it results in a bonding of similar and dissimilar components and ultimately affects the distribution of components or phases in the final sintered compact.

The degree to which diffusion occurs and mass transport results in the initial sintering stage is dependent on a number of factors, i.e.:

(1) Surface energy of phases
(2) Plastic flow which has, or is, occurring. This gives rise to pipe diffusion along dislocation cores.
(3) The degree to which the various diffusion paths operate under the experimental conditions.
(4) The geometry of the contact area between pairs of spheres being sintered.
(5) The diffusion coefficients of phases present.

In the consideration of diffusion sintering models it is customary to consider the geometry of the system as either "pairs of contacting spheres" or "contacting spheres and plates". In our case the "pairs of contacting spheres" is applicable and will be considered.[9,10,11,12]

In general, material transport is expressed in terms of the reverse flux of lattice vacancies. Various possible sites for vacancy creation and annihilation and several types of diffusion paths are possible, as shown in Figure 2, with arrows showing the direction of vacancy diffusion. Mass transport will, therefore, be in the reverse direction.

From Figure 2 we see that at least five possible paths exist for material transfer when initial (solid state) sintering occurs between pairs of spheres. Of these, the first four paths are generally considered to be most effective during the initial stage of sintering. The geometric changes which occur between pairs of spheres for the first four cases are given in Figure 3. These are not the only possible changes which can occur since the limitation to the number of processes in a system is that a free energy decrease accompany the configuration change.

The nomenclature used for the sintering models in Figure 3 is as follows. A pair of spheres of radius R sinter to form a neck of radius x, such that the contact area between spheres is πx^2. The outer surface of this neck is of axial length ρ. The spherical surface is approximated by $x^2/2R = Y$.

The standard approach to the description of a sintering model is to express the volume change $(\frac{dV}{dt})$ in terms of the geometric change which

is fixed by assuming which vacancy sinks and sources are operating.[13,14] This in turn fixes the vacancy path, and therefore, the material transport direction. As an example, only the configuration change in cases I and II (Figure 3) utilize the grain boundary as a vacancy sink. In the first case (I) two vacancy paths (a) and (b) are possible. Path (a) represents bulk diffusion in that vacancies from the neck surface migrate into the bulk of the sphere and then into the grain boundary being formed. Also, vacancy motion occurs via path (b) which consists of vacancy migration from the neck surface via boundary and surface diffusion to the newly formed grain boundary between the two spheres. The net transport of material will be in the reverse direction, i.e. from the region of the grain boundary formed to the neck surface, resulting in the neck growth as shown.

In Case II one vacancy path is assumed operative from the grain interior (acting as a source) to the grain boundary (acting as a sink), i.e. bulk diffusion. The result here is that neck surface growth will not occur but grain boundary growth will, as shown.

For the four transport models considered applicable during the initial stage of sintering there is an implicit assumption that all vacancy sources and sinks are not simultaneously operative. This results in the ability to interpret quantitatively the observed effects. However, the limitations of this approach should be recognized. In particular the ability of any one source or sink to change its character and subsequent operation as a function of thermal cycling must be considered. Table IV lists the relations assumed in each model.

The rate of volume diffusion (dV / dt) for case I is expressed at the formed grain boundary. The boundary area is x^2 and $dV / dt = x^2 \, dy/dt$ Next, the continuity equation, $y = x^2 / 4R$ is determined by equating the inner and outer volume of the shaded axes. For the other three cases the continuity equation expressed the relation between neck growth and shrinkage (case II) or between neck growth and surface curvature (case III and IV).

For a single component system the vacancy diffusion flux is driven by the gradient of the chemical potential which results from change in surface curvature. The highest vacancy concentration is then found at the surface of the neck, i.e. the nonspherical segment which connects the two spheres. The shape of the neck surface is important since the excess vacancy concentration under a curved surface is expressed by:

$$\Delta C = C_o \frac{\gamma \Omega^3}{kT\rho} \qquad (8)$$

where

ΔC = change in vacancy concentration

C_o = vacancy concentration under a flat surface (in bulk)

γ = surface energy

δ^3 = vacancy volume

k = Boltzmann's constant

T = absolute temperature

$\rho = \frac{1}{1/R_1 + 1/R_2}$ where $R_1 + R_2$ are maximum and minimum possible radii of curvature. This is the effective axial length from vacancy source (neck) to center of boundary formed.

Once the excess vacancy concentration (ΔC) is known, the vacancy flux (J) per unit length can be computed from:

$$J = 4\pi D_v \Delta C \quad \text{vacancies/sec} - \text{cm} \qquad (9)$$

where D_V = vacancy diffusion coefficient

The length over which vacancy diffusion must occur is from source to sink and this is, in effect, equal to ρ in Equation (8). Then if the volume of each vacancy diffused is δ^3 the total volume of vacancies diffused will be:

$$J\rho\delta^3 = 4\pi D_v \Delta C \rho \delta^3 \qquad (10)$$

Equation (10) above represents the volume of vacancies diffused per unit time and, therefore, the volume of material transfer per unit time. This amount of material transfer per unit time is equal to the rate of volume diffusion (d V /dt), i.e. volume change.

Therefore, for case I $y = x^2/4R$

$$\frac{dV}{dt} = \pi x^2 \frac{dy}{dt}$$

$$dy = 2x\frac{dx}{4R} = \frac{x\,dx}{2R}$$

$$\frac{dV}{dt} = \frac{\pi x^2}{2R}\frac{x\,dx}{dt} = J\rho\delta^3 = 4\pi D_v \Delta C \delta^3 \rho$$

$$x^3 dx = 8R D_v \Delta C \delta^3 \rho\, dt$$

substituting $\Delta C = C_0 \gamma \delta^3 / kT$

$$x^3 dx = 8R D_v \frac{C_0 \gamma \delta^3 \rho}{kT\rho} \delta^3 dt$$

$$\int x^3 dx = \int 8R D_v C_0 \gamma (\delta^3)^2 dt / kT$$

$$x^4 = 32 R D_v C_0 \gamma (\delta^3)^2 t / kT \qquad (11)$$

Again: X = radius of neck which results during initial sintering

R = initial radius of sintered spheres

t = time of sintering

T = temperature of sintering

δ^3 = vacancy volume

k = Boltzmann's constant

D_v = diffusion coefficient for vacancies

γ = surface energy

C_0 = vacancy concentration under a flat surface

We have expressed in Equation (11) the neck radius which forms due to material transport during sintering at temperature (T) for a time (t). As shown, three parameters D_V, γ, and C_o must be determined for the

conditions under which sintering occurs if a rigorous analysis of initial sintering effects is to be made. It is toward a determination of these constants that the point defect studies of contract NAS8-24952 are aimed.

VII. SURFACE ENERGY (γ)

From the discussion in Sections IV and V it is apparent that the surface energy (γ) will not be a constant for the entire sintering process but will, due to thermal faceting and adsorption, tend to some lower energy value. This is due to the fact that we will be heating in vacuum in the presence of active residual gases (O). It is also expected that the presence of residual gases will affect the faceting process. Therefore, only via experimental determination under actual and simulated vacuum and residual gas environments can we expect to obtain an unambiguous quantitative value for (γ).

VIII. VACANCY CONCENTRATION UNDER A FLAT SURFACE (C_o)

The C_o of interest in most sintering procedures will simply be the bulk vacancy concentration. This value could be determined from a knowledge of the energy of formation of a vacancy (E_V^F) and the temperature T of sintering, i.e.:[16]

If we assume that our system consists of N atoms at some temperature T then we let E_V^F equal the energy required to remove an atom from a normal site in the system and place it in the surface. Also let n equal the number of such vacancies formed. The total increase in internal energy (E) due to vacancy formation will be nE_V^F.

The entropy of mixing of N atoms and n vacancies in a system of N + n sites is given by:

$$S = k \ln [(N+n)!/N!n!] \qquad (12)$$

where k = Boltzmann's constant

The free energy, F, of the system with n defects (vacancies), relative to the free energy of a perfect (defect free) system is:

$$F = E - TS \qquad (13)$$

or

$$F = nE_V^F - Tk \ln [(N+n)!/N!n!]$$

$$F = nE_V^F - Tk [\ln(N+n)! - \ln N! - \ln n!]$$

or

using Sterling's approximation $\ln X! = X \ln X - X$

we obtain $$F = nE_V^F - kT[(N+n)\ln(N+n) - n\ln n - N\ln N] \quad (14)$$

The equlilbrium value of n is that for which d F / d n = 0

or $$\frac{dF}{dn} = 0 = E_V^F - kT[\ln(N+n) + 1 - \ln n - 1]$$

$$-\frac{E_V^F}{kT} = \ln n - \ln(N+n)$$

$$e^{-E_V^F/kT} = \frac{n}{N+n} \qquad \text{for } N >> n$$

$$\frac{n}{N} = e^{-E_V^F/kT} = C_o \quad (15)$$

Equation (15) represents the concentration of vacancies in a one component system, and can be substituted in the expression for the change in vacancy concentration (Δ C). For our experiments it is anticipated that two-component systems will be used. The existing condition will, therefore, be somewhat complicated in that two individual vacancy concentrations will be present and will have an effect on Δ C. Also, two energies of formation, i.e. E_V^{F1} and E_V^{F2} will be involved and for the temperature of sintering (T) two vacancy concentrations will be present C_o^1 and C_o^2. This condition will in turn complicate the vacancy source and sink considerations in that the component with the lower E_V^F, will, for a given temperature, possess a higher concentration of vacancies. This will result in a vacancy concentration gradient which exists across the specimen "neck". This gradient may, if large enough, override all other vacancy sink-source considerations. Therefore, a determination of the vacancy concentration as a function of temperature at or just below specimen surfaces must be determined for each component to be utilized in the sintering process. This can be determined via the series of experiments outlined in contract NAS8-24952.

IX. THE VACANCY DIFFUSION COEFFICIENT (D_V)

Most studies into the diffusion of vacancies in a solid have been conducted via high temperature quenching and resistivity experiments.[15] The quenching of a solid results in a supersaturation of vacancies and subsequent low-temperature annealing provides the energy for migration and annihilation at sinks. This process results in a change (decrease) in electrical resistivity which can then be used to determine the half life of vacancies and their diffusion coefficients. For the interpretation of effects expected in the initial stage of sintering an approach which utilizes a supersaturated vacancy situation in the individual components is not accurate.

Thermal equilibrium will be achieved throughout the solid-spherical particles of the two phases in our system. This equilibrium, reached after some time at the sintering temperature, will have the following characteristics:

(1) In the bulk of the solid spheres, a vacancy concentration (C_o) will be reached. The value of (C_o^1) in one phase (sphere) will not be equal to (C_o^2) that in the second. Although vacancy sinks and sources will be active in the bulk, the equilibrium condition dictates that the net number of vacancies will not change if temperature remains constant. This further dictates that a variable vacancy sink mechanism is not operative and, therefore, that vacancy sinks whose effectiveness changes with time can be ignored as inoperative, i.e. dislocation loops, tetrahedra, etc.

(2) Across the region of the neck (boundary) formed (or forming) between the two spheres, a definite vacancy gradient will exist, causing a net flow of vacancies from one sphere to the other. This flow will be present simply because of the concentration differences C_o^1 and C_o^2 and is not limited by the active action of sinks.

Under the conditions of thermal equilibrium the diffusion coefficient (D_V) may be given by:

$$D_v = A_v^M Z \nu b^2 \exp(E_v^M/kT) \qquad (16)$$

where A_V^M = the entropy of vacancy migration

Z = the coordination number (12 in fcc)

ν = the atomic frequency 10^{13} sec^{-1}

b = the atomic diameter

E_V^M = the activation energy for vacancy migration

The constants A_V^M and E_V^M have been determined for a large number of metals and can be obtained from the literature. However, this has been done under experimental conditions which assume either a fixed vacancy sink and/or a variable vacancy sink condition. Therefore, before a choice of constants can be made, the type of mechanisms involved in the system must be determined. This can be done via the annealing and heat treating studies by a determination of the process kinetics. That is, the fixed vacancy sink condition reflects itself as a 1st order reaction and the variable vacancy sink condition as a second or higher order reaction.

X. SUMMARY

It has been the intent of this paper to point out those areas of research that are important in the overall study of liquid phase sintering in space. From a consideration of the various research areas, several concepts relevant to materials experiments in space emerge. The first of these concepts is that materials processes that involve a liquid phase are most likely to be influenced by the details of gravitational fields. This is perhaps self-evident. Perhaps more important is a realization that most of the possible metallurgical processes proposed for space experiments will be influenced by the details of the gaseous environment. For instance, the high percentage of O and O_2 in the residual gases of the space vacuum will have significant effects on the results.

The close or direct connection between materials processes employing a liquid phase and the residual gases of the space vacuum occurs through a consideration of surface free energies. The behavior of a liquid phase in the absence of a gravitational field will be controlled by the surface energy terms. That is, surface energy terms will predominate and be responsible for driving any reactions or establishing the equilibrium states. However, surface energies are significantly affected by the gaseous environment through the process of adsorption and consequently the effect of the gaseous environment on such energy terms must be determined.

For the proposed experiments on sintering, it was pointed out that a two-step process is involved. In the initial stage, where only solid and gaseous phases are involved, a significant amount of material transport is expected to occur. In theoretically considering the mechanism involved, the conclusion is reached that the vacancy concentration is a function of the surface energy terms. Also, the phenomenon of thermal faceting is expected and is shown to be a function of surface energies. Specific relations between these mechanisms must be determined for the space environment. In the final stage of the sintering experiment, the liquid phase makes its appearance and the phenomenon of wetting is of crucial importance. Again, wetting is a function of

surface energies and the important relations must be determined.

Figure 4 is an attempt to show the connections between the various mechanisms involved in liquid phase sintering in the space environment. At best it is incomplete and represents a first attempt, on our part, of such a representation. We feel these inter-relationships to be crucial for the space experimental program.

REFERENCES

1. Whalen, T. J. and Humenik, M., Jr., Trans. AIME, 218,952 (1960)

2. Humenik, M., Jr. and Whalen, T. J., Chapter 2 in "Cermets", J. R. Tinklepaugh and W. B. Crandall, Editors, Reinhold Publishing Corp., 1960

3. Handbook of Geophysics and Space Environment, AFCRL 1965

4. Progress in Reaction Kinetics, Vol. 1, G. Porter, ed. (Pergamon, New York, 1961)

5. Gibbs, J. W. "The Collected Work of J. Williard Gibbs," Vol. 1, p. 223 ff, Yale University Press, New Haven, Conn. (1948)

6. Moore, A. J. W., Metal Surfaces; ASM Conf. Proc. p 155 (1962)

7. Young, F. W. and Gwathmey, A. T., J. Appl. Physics 31, 225 (1960)

8. Elam, C. F., Trans. Faraday Soc. 32, (1936)

9. Marshall, P. A. Jr., Enright, D. P., and Weyl, W. A., Proc. Sym. Reactivity of Solids, Gothenburg, pp 273 (1952)

10. Gray, T. J., J. Am. Ceram. Soc. 37, pp 534 (1954)

11. Burke, J. E. J. Am. Ceram. Soc. 40, pp 80 (1957)

12. Walker, R. F., J. Am. Ceram. Soc. 38, pp 187 (1955)

13. Kingery, W. D. and Berg M., J. Appl. Phys. 26, pp 1205 (1955)

14. Alexander B. H. and Balluffi, R. W., J. Metals, 2 pp 1219, (1950)

15. Cottrell, A. H., Theoretical Structural Metallurgy, St. Martins Press, New York - 1st Edition (1960)

16. Coble, R. L., J. Am. Ceram. Soc., Vol. 41, No. 2 (1958)

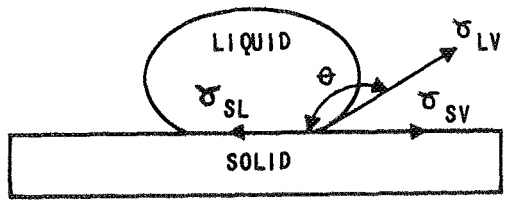

Figure 1 LIQUID DROP ON SOLID SUBSTANCE

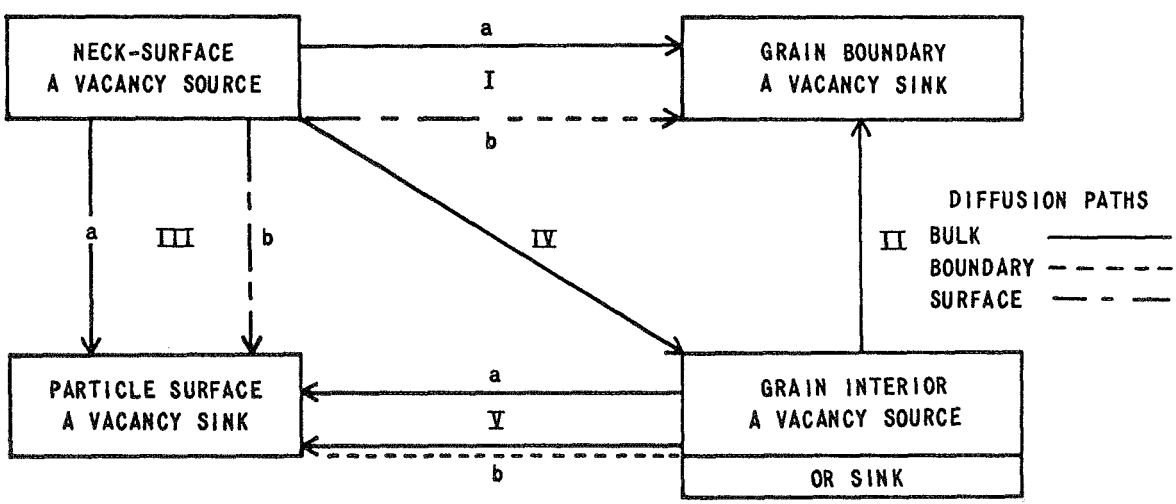

Figure 2 VACANCY SOURCES, SINKS AND PATHS FOR SINTERING BETWEEN PAIRS OF PARTICLES

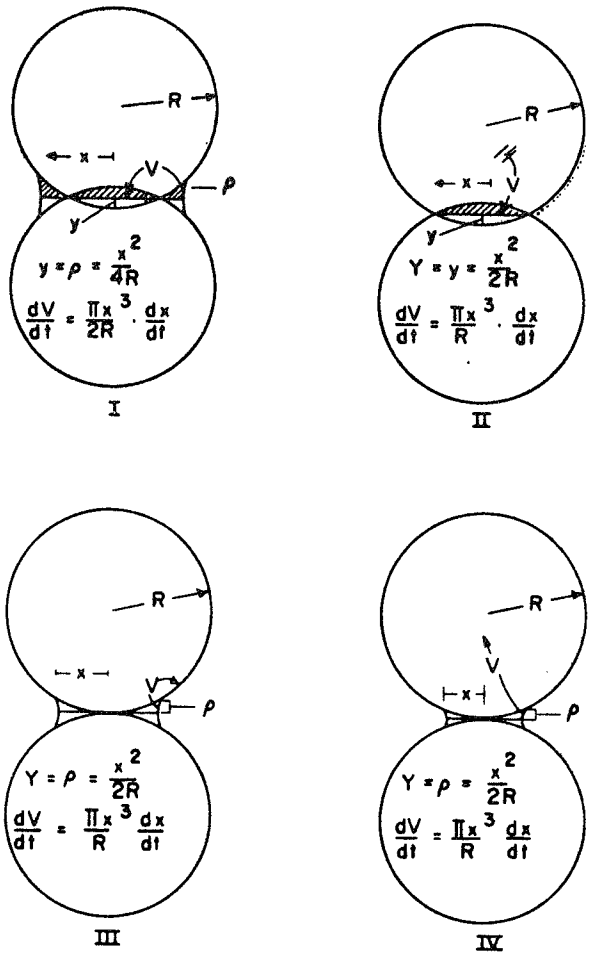

Figure 3 GEOMETRIC EXPRESSIONS FOR SINTERING BETWEEN PAIRS OF SPHERES

where: R = radius of spheres

X = radius of neck

ρ = axial length of neck outer surface

Y = spherical surface

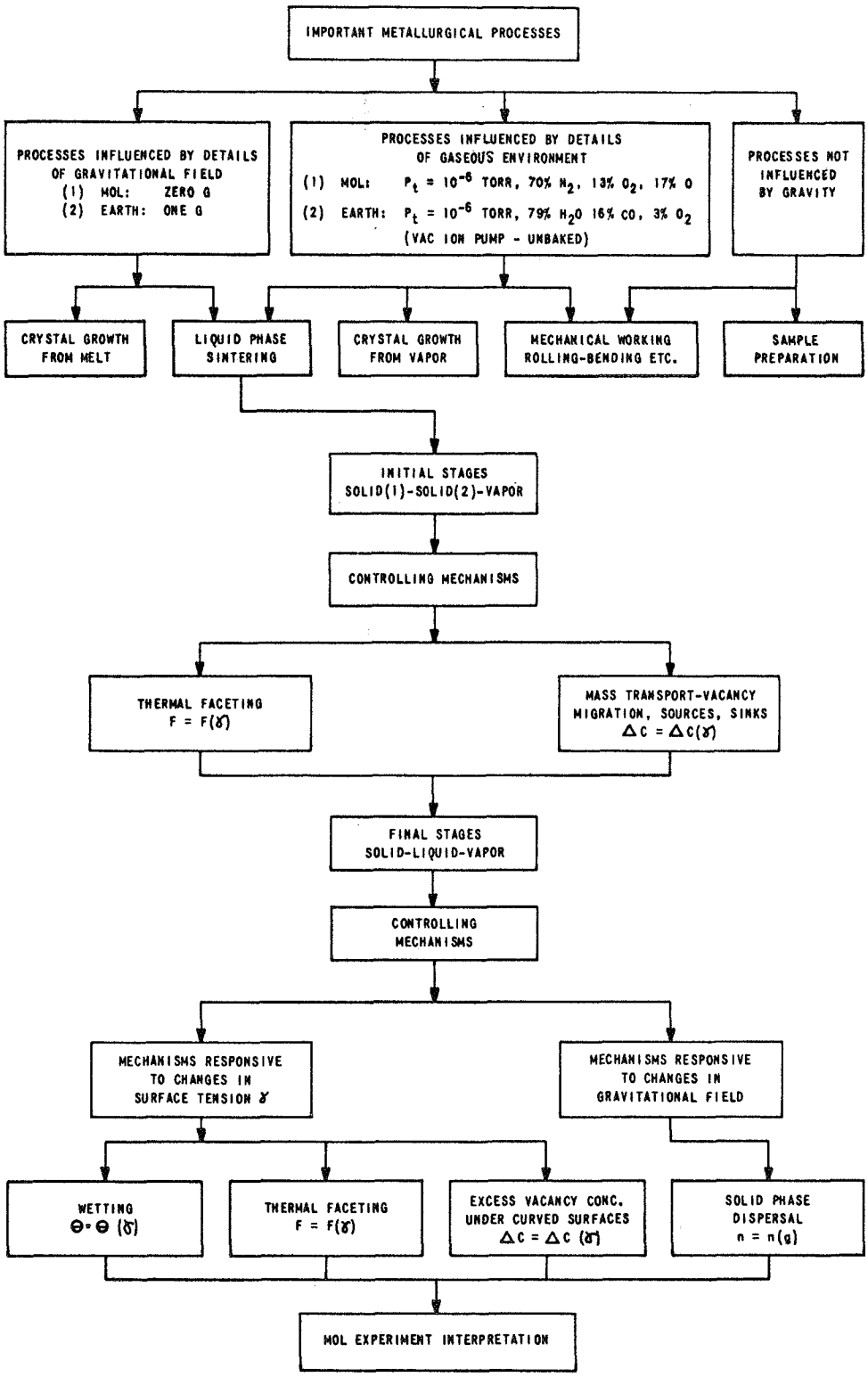
IMPORTANT METALLURGICAL PROCESSES
PROCESSES INFLUENCED BY DETAILS OF GRAVITATIONAL FIELD
(1) MOL: ZERO G
(2) EARTH: ONE G
PROCESSES INFLUENCED BY DETAILS OF GASEOUS ENVIRONMENT
(1) MOL: $P_t = 10^{-6}$ TORR, 70% H_2, 13% O_2, 17% O
(2) EARTH: $P_t = 10^{-6}$ TORR, 79% H_2O 16% CO, 3% O_2
(VAC ION PUMP - UNBAKED)
PROCESSES NOT INFLUENCED BY GRAVITY
CRYSTAL GROWTH FROM MELT
LIQUID PHASE SINTERING
CRYSTAL GROWTH FROM VAPOR
MECHANICAL WORKING ROLLING-BENDING ETC.
SAMPLE PREPARATION
INITIAL STAGES SOLID(1)-SOLID(2)-VAPOR
CONTROLLING MECHANISMS
THERMAL FACETING $F = F(\delta)$
MASS TRANSPORT-VACANCY MIGRATION, SOURCES, SINKS $\Delta C = \Delta C(\delta)$
FINAL STAGES SOLID-LIQUID-VAPOR
CONTROLLING MECHANISMS
MECHANISMS RESPONSIVE TO CHANGES IN SURFACE TENSION δ
MECHANISMS RESPONSIVE TO CHANGES IN GRAVITATIONAL FIELD
WETTING $\Theta = \Theta(\delta)$
THERMAL FACETING $F = F(\delta)$
EXCESS VACANCY CONC. UNDER CURVED SURFACES $\Delta C = \Delta C(\delta)$
SOLID PHASE DISPERSAL $n = n(g)$
MOL EXPERIMENT INTERPRETATION

Figure 4 IMPORTANT METALLURGICAL PROCESSES

TABLE I

PROPERTIES OF LIQUID METALS AND CARBON SELECTED FOR EXPERIMENTS ON THE EFFECT OF DENSITY ON LIQUID PHASE SINTERING

	Melt Pt. °C °F	Density gm/cm^3 at °C	C Solubility W/O at °C	Surface Energy $ergs/cm^2$
Carbon	3727	2.22/-	--	--
Silver	960/1760	10.49/960	.0012/1600	923.0
Aluminum	660/1220	2.37/660	Trace	914.0

TABLE II

EFFECT OF DECREASING ONE SURFACE ENERGY ON CONTACT ANGLE, MAINTAINING OTHERS CONSTANT

Decreased Surface Energy	Change in Contact Angle	
	Initial Angle	Initial Angle
	$<90°$	$>90°$
Liquid-Vapor	Decrease	Increase
Solid-Vapor	Increase	Increase
Solid-LIQUID	Decrease	Decrease

TABLE III

PROPERTIES OF LIQUID METALS AND CARBON SELECTED FOR EXPERIMENTS ON THE EFFECT OF SURFACE ENERGY ON LIQUID PHASE SINTERING

	Melt Pt. °C °F	Density gm/cm^3 at °C	Carbon Solubility	Surface C. Energy ergs/cm^2
Carbon	3727	2.22/ -	--	--
Tin	232/449	6.83/409	Trace	579.5
Zinc	420/787	6.92/420	Trace	784.8

TABLE IV

Case	Vacancy Source	Vacancy Sink	dV/dt	Continuity Equation	Produces
I	Neck	Boundary	$\pi x^2 dy/dt$	$y = x^2/4R$	Neck growth and shrinkage
II	Dislocations	Boundary	$\pi x^2 dy/dt$	$y = x^2/2R$	Neck growth and shrinkage
III	Neck	Surface	$2\pi x\rho dx/dt$	$\rho = x^2/2R$	Neck growth
IV	Neck	Dislocation	$2\pi x\rho dx/dt$	$\rho = x^2/2R$	Neck growth